

Some remarks on the foundations of stochastic time-dependent current-density functional theory for open quantum systems

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We clarify some misunderstandings on the time-dependent current density functional theory for open quantum systems we have recently introduced [M. Di Ventra and R. D’Agosta, Phys. Rev. Lett. **98**, 226403 (2007)]. We also show that some of the recent formulations attempting to improve on this theory suffer from some inconsistencies, especially in establishing the mapping between the external potential and the quantities of interest. We offer a general argument about this mapping, showing that it must fulfill certain “dimensionality” requirements.

Experience teaches us that no physical system can be considered as completely closed, in the sense that some degrees of freedom are either too many to consider explicitly, or their microscopic features are not of interest, and only their macroscopic thermodynamic properties are of importance. These degrees of freedom are then treated as baths or reservoirs of the system of interest, making the latter “open”. Nonetheless, the theory of open quantum system is relatively new, starting with the pioneering works by Zwanzig and Nakajima,^{1,2} who worked out the theory in terms of the statistical operator (density matrix), and more recently with the formulation of the theory of open quantum system in terms of a state vector (“wavefunction”).^{3,4}

In parallel, another theory, Density Functional Theory (DFT), developed since the first papers by Kohn and co-workers,^{5,6} has changed the way we think in terms of many-body quantum mechanical systems. Indeed, the successes of DFT are countless, and the theory has now become a standard for many calculations of electronic structure, electron transport, materials properties, and chemical reactions.^{7–12}

The attempt to bring together the two theories appears therefore completely natural.^{13–19} In particular, the present authors have proved a theorem that establishes a one-to-one correspondence between a vector potential acting on an open quantum system and its current density,^{14,15} a theorem that was later extended to the correlated motion between electrons and (in principle quantum) ions,^{16,20} This theory, which we named stochastic time-dependent current-DFT (STDCDFT), then allows for the solution of a many-body open quantum system with effective single-particle equations, a significant computational sim-

plification.

Although still in its infancy, STDCDFT for open quantum systems has received a certain amount of attention, especially for its promise to expand the field to systems previously inaccessible within standard DFT. However, there is also some confusion regarding its foundations which is mostly evident in recent developments, for instance a new result that shows how in principle we can mimic the dynamics of an open quantum system by reverting to the analysis of a closed quantum system made of non-interacting particles.^{17,18} This result would further dramatically reduce the computational cost for evaluating the dynamics of the open quantum system.

The reason for this reduction is simple. In general, the open quantum system could be described in two ways. On the one hand, we can use the many-body statistical operator, or the single-particle reduced density matrix. However, for large systems, the number of degrees of freedom, i.e., the dimensionality of the operator we need to consider, scales badly although some schemes can be devised to cure this scaling.²¹ On the other hand, a formulation in terms of a stochastic state vector is computationally cheaper than a density matrix one, but nonetheless it requires the consideration of a statistical ensemble of replicas of the system. Larger the ensemble, finer will be the physical information we can extract from the dynamics. Instead, if we could describe the dynamics of the open system with a closed non-interacting system, we would have reduced a complex and expensive problem to a size similar to that we usually tackle with our present computational means.

Obviously, a situation common in DFT—we cannot expect to have access to the complete physical information about the open quantum system. We must accept that our non-interacting *doppelgänger* will be able to describe only some quantity of choice, normally either the single-particle density or the single-particle current density. In principle, any other physical observable can be extracted provided we know its expression in terms of these “fundamental” quantities. However, in practice,

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we rarely know how to write such observables in terms of the density or the current density, thus limiting the range of physical quantities that can be actually computed. Our goal for this paper is to both clarify some of the theoretical foundations of STCDFT that do not seem to have been appreciated in the literature, as well as to show that some of the recent attempts to extend this theory^{17,18} suffer from inconsistencies, in particular those related to the mapping between external potentials and the basic quantities of any density functional theory.

Let us then start by noting that the choice about which quantity we want to base our theory on is usually made *a priori*. For this reason we usually talk about DFT or Current-DFT.^{10,22} For closed systems, Current-DFT is regarded as a more complete theory than DFT since, via the continuity equation, one can calculate the single particle density starting from the single particle-current density. The situation is instead more complex in open quantum systems since, as we are going to show in the following, *prima facie* the continuity equation would seem not to uniquely determine the single-particle density, given the single-particle current density.

Let us then begin by recalling that in the theory of open quantum systems, the equation of motion for the ensemble-averaged particle density, $n(r, t)$, is given by (see, e.g.,²³)

$$\partial_t n(r, t) = -\vec{\nabla} \cdot \vec{j}(r, t) + \mathcal{F}_B(r, t) \quad (1)$$

where $\mathcal{F}_B(r, t)$ describes the density modulation induced by the presence of the bath(s) and $\vec{j}(r, t)$ is the ensemble-averaged current density*. Eqn 1 can be obtained from the master equation of motion for the density matrix, $\hat{\rho}$ ($\hbar = 1$)

$$\partial_t \hat{\rho}(t) = -i \left[\hat{H}(t), \hat{\rho}(t) \right] + \int_{t_0}^t dt' K(t, t') \hat{\rho}(t'). \quad (2)$$

Here, $K(t, t')$ is a memory kernel that describes the action of the bath(s) on the system—provided it is chosen to preserve the positivity of the density matrix at any given time—^{1,2,19,24,25} and $\hat{H}(t)$ is the Hamiltonian of the system that evolves under the action of an external vector potential (possibly time dependent), $\vec{A}(r, t)$, and in the presence of a particle-particle interaction operator \hat{W} ,

$$\hat{H}(t) = \frac{1}{2m} \sum_i \left(\hat{p}_i + e\vec{A}(\hat{r}_i, t) \right)^2 + \hat{W} \quad (3)$$

We work here in a gauge where the scalar potential has been set to zero at all times.

In general, little is known about the term \mathcal{F}_B appearing in the continuity equation (1). Although not strictly necessary for the considerations we make later, it would be useful if \mathcal{F}_B could be written as the divergence of some current. This

would immediately imply the conservation of the total number of particles. Recently, Gebauer and Car have shown that this is indeed the case in the Markov approximation for certain couplings between the system and the environment.^{26,27} More recently a formal condition on current conservation and its use to test the validity of the approximations made to arrive at the master equation has been proposed.²⁸ If \mathcal{F}_B is the divergence of some current—this extra current being generated by the exchange of momentum and energy with the external environment—then the continuity equation assumes the usual physical meaning and particle number conservation is guaranteed. Moreover, one could assume that

$$\mathcal{F}_B = -\nabla \cdot \left(\frac{e\vec{C}(r, t)}{m} n(r, t) \right), \quad (4)$$

where without loss of generality we have written the extra current as $en(r, t)\vec{C}(r, t)/m$. If this were the case, the total current $\vec{j}_T(r, t) = \vec{j}(r, t) + en(r, t)\vec{C}(r, t)/m$ fulfills the standard continuity equation,

$$\partial_t n(r, t) = -\nabla \cdot \vec{j}_T(r, t). \quad (5)$$

In the total current, $\vec{C}(r, t)$ appears then to play the role of an extra vector potential, effectively inducing a diamagnetic current in the system, $en(r, t)\vec{C}(r, t)/m$. Interestingly, in Ref.¹⁷ $\vec{C}(r, t)$ has been dubbed “leakage potential”, although we would like to point out that its definition from eqn 4 essentially prevents any leakage, i.e. loss of particles, from the system.

In standard TDCDFT for closed quantum systems, where the extra term in Eq. (1) is not present, i.e., $\mathcal{F}_B(r, t) = 0$, the continuity equation establishes an important link between the single-particle current density $\vec{j}(r, t)$ and the single-particle density $n(r, t)$. Indeed, this equation allows for expressing the latter in terms of the former via a simple time integration. This seems a trivial point, but let us clearly state it: The continuity equation, when $\mathcal{F}_B(r, t) = 0$ can be used together with the initial conditions to *uniquely* determine the single-particle density given the single-particle current density. The basic theorem of TDCDFT therefore establishes a one-to-one mapping between the current density and the vector potential applied to the system, once the initial conditions are provided.^{10,12,29} In fact, whenever one discusses the uniqueness of the mapping between the single-particle density and single-particle current density with the external vector potential, it is implicitly understood that the particle density is obtained from the current density via the continuity equation.

The situation becomes a bit trickier whenever $\mathcal{F}_B(r, t) \neq 0$. In this case one needs the expressions of both \vec{j} and $\mathcal{F}_B(r, t)$ to be able to determine the single-particle density. However, written in this way the problem corresponds to the solution of a linear differential equation with non-constant coefficients. Then,

*In this theory we do not allow for the system to exchange particles with the environment.

if one knows \mathcal{F}_B we just need to perform a simple time integration. From a TDCDFT formulation of the theory then, as it has been shown,^{14,15} one can build a one-to-one mapping between the (average) current density and the external vector potential, provided the initial condition and the bath operators are fixed.

Here we stress that the inclusion in the mapping of the density along with the current density—as for example it has been tried in Ref.¹⁷—is not just redundant, but simply incorrect. Indeed, we will show in the following that the mapping between the set of current and particle densities and the *vector* potential is not unique. Our argument can be extended to other cases. For example, along the same lines we can prove that the mapping between the current density and the *scalar* potential cannot be one-to-one. One of us (RD) has already presented another proof of the same result, in particular showing that the current density is in general non-V-representable.³⁰ This, therefore, precludes the access to all components of the current density by standard TDDFT. Our following argument also sets a necessary condition for building any density functional theory, in terms of establishing a one-to-one correspondence between two physical quantities. This condition states that the two quantities must have the same “dimensions”: a vector with a vector, a scalar with a scalar and so on. Any other mapping will be either redundant or wrong.

That this point is still not clear in the community is evident for example in the thesis of Theorem 1 of Ref.¹⁷ where it is stated that there exists a one-to-one correspondence between a vector potential and the set of functions given by the current and particle densities. The Authors of that work go also as far as clearly stating in their discussion of the content of Theorem 1 that their aim is to consider the particle density on the same footing as the current density. However, this statement cannot be correct as a simple mathematical characterization of the functional spaces connected by this mapping shows. If the particle and current densities were *independent* functions, then they would belong to a 4-dimensional functional space. This amounts to saying that $\mathcal{F}_B(r, t)$ is not completely determined by the sole knowledge of $n(r, t)$ and $\vec{j}(r, t)$. Indeed, if $\mathcal{F}_B(r, t)$ was determined by the sole knowledge of the single-particle densities, then we could use the continuity equation (1) as a non-linear differential equation for the density and by solving it, obtain $n(r, t)$ in terms of the initial conditions and $\vec{j}(r, t)$. Since a general vector potential is a vector of three independent functions, Theorem 1 in¹⁷ would imply that a 4-dimensional functional space formed by the density plus the three components of the current density is locally homeomorphic to a 3-dimensional functional space spanned by the vector potential. This is obviously incorrect.

The solution to this inconsistency is that the continuity equation (1) is indeed a non-linear equation in the particle and current densities from which the particle density can be obtained starting from the current density, once the bath operator and ini-

tial conditions have been fixed.^{14,15} This amounts to saying that $\mathcal{F}_B(r, t)$ is a functional of $n(r, t)$ and $\vec{j}(r, t)$, or better of $\vec{j}(r, t)$ alone, and that equation (1) admits a unique physical solution.

In fact, we can provide a simple counter argument to the existence of a mapping between the vector potential and the set of functions given by the particle and current densities. Consider the extremely simple case in which the response functions of the system are local in time and constant in space, and that the (full) response is linear. This case is obviously extremely simplified. However, to provide a counterexample to a theorem we do not need to discuss more complex cases. For this oversimplified system we can write the following response equations (for simplicity, in the next few equations we drop the spatial and temporal dependence of j and n)

$$\begin{pmatrix} j_x \\ j_y \\ j_z \\ n \end{pmatrix} = \hat{\Gamma} \begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} \quad (6)$$

where Γ is a 4×3 matrix of constant coefficients of the system response. The existence of a one-to-one mapping between the particle and current densities and the vector potential would then suggest that we can write a similar equation, starting from the particle and current densities

$$\begin{pmatrix} A_x \\ A_y \\ A_z \end{pmatrix} = \hat{\Gamma}' \begin{pmatrix} j_x \\ j_y \\ j_z \\ n \end{pmatrix} \quad (7)$$

where now Γ' is a 3×4 matrix. Combining these results it follows that

$$\hat{\Gamma}\hat{\Gamma}' = 1_4; \hat{\Gamma}'\hat{\Gamma} = 1_3, \quad (8)$$

where 1_N is the $N \times N$ identity matrix.

We can now easily prove that either the current and particle densities are not independent (and therefore the mapping is indeed redundant), or the mapping between the current and particle densities and the vector potential is not one-to-one. Due to the particular structure of eqn 6, we can invert the relations between the current density and the vector potential and express the latter in terms of the former. Since this is in principle a 3-by-3 system of linear equations, it admits always at least one solution. Then, we can use the results found in this way in the equation for the particle density, therefore expressing the latter in terms solely of the current density, thus proving the mapping redundant.

On the other hand, since eqn (7) is a system of 3 equations in 4 variables, we can always find two distinct sets of current and particle densities providing the same vector potential. Therefore an infinite number of solutions can be found. To show this we proceed in this way: Assume that \vec{j}_0, n_0 are

a set of current and particle density, and that \vec{A}_0 is the resulting vector potential obtained from (7). Now let us consider the particle density $n = n_0 + \Delta n$. We want to show that we can find another current density $\vec{j} = \vec{j}_0 + \Delta \vec{j}$ which together with n gives, via (7), the same vector potential. Since Δn is arbitrary we can choose as initial condition $\Delta n(r, t = 0) = 0$, therefore the two sets of current and particle densities do satisfy the same initial conditions. To prove our point, it is enough to prove that the system of equations

$$\hat{\Gamma}' \begin{pmatrix} \dot{j}_{0,x} \\ \dot{j}_{0,y} \\ \dot{j}_{0,z} \\ n_0 \end{pmatrix} = \hat{\Gamma}' \begin{pmatrix} \dot{j}_x \\ \dot{j}_y \\ \dot{j}_z \\ n \end{pmatrix}, \quad (9)$$

or the equivalent

$$\hat{\Gamma}' \begin{pmatrix} \Delta j_x \\ \Delta j_y \\ \Delta j_z \\ \Delta n \end{pmatrix} = 0 \quad (10)$$

admits at least one solution. This is again trivially true, since this is a system of 3 equations in 4 variables. We can now assume the density Δn assigned and find, if the 3x3 submatrix of $\hat{\Gamma}'$ is invertible, the corresponding current density that satisfies eqn (10). If that submatrix of $\hat{\Gamma}'$ is not invertible, then we will be able to find more than one solution for $\Delta \vec{j}$, thus reinforcing our statement. The solution found in this way can also be made to fulfill the initial condition $\Delta \vec{j}(r, t = 0) = 0$.

It is also worth pointing out that the standard proof of the theorem for STDCDFT¹⁴, as well as that of the theorem of standard TD-CDFT,²⁹ does *not* require that the particle density in the auxiliary system is equal to the particle density in the original one. Indeed, in the standard TD-CDFT proof one uses the standard continuity equation to *infer* the equality between the two densities. In our proof¹⁴, we postulated it from the uniqueness of the solution of the non-linear continuity eqn (1), with $\mathcal{F}_B(r, t)$ a functional of the current density. In those proofs one only needs to determine the n -th time derivative of all quantities, and only the $(n + 1)$ -th time derivative of the vector potential. The n -th time derivative of the particle density is obtained from eqn (1) (or, in a closed system from the same equation with $\mathcal{F}_B = 0$). That equation, however, does not contain any $(n + 1)$ -th time derivative. Therefore, the equation for the vector potential in the auxiliary system we use in our proof¹⁴ is still a recursive relation, with a unique solution provided the initial conditions. The theorem then guarantees the one-to-one correspondence between external vector potential and ensemble-averaged current density, leaving open the (possibly quite difficult) task of obtaining the ensemble-averaged density from the current density, when the continuity equation is given by eqn (1).

This one-to-one mapping, implies that \mathcal{F}_B is a functional of the current density $\vec{j}(r, t)$, the initial conditions and the cou-

pling between the system and the environment. This ultimately implies that— by the knowledge of this functional—we could uniquely determine the single particle density. This is however a common situation with DFT. The theorems of DFT offer a solid foundation for certain calculations by guaranteeing that one quantity can be exactly obtained from a *doppelgänger* system. The other physical quantities have to be derived from the first one, usually a difficult—if not hopeless—task.

We now want to critically examine Theorem 3 in Ref.¹⁷, where the main result of that paper is presented: it is possible to construct a closed non-interacting quantum system that mimics the dynamics of $n(r, t)$ and $\vec{j}(r, t)$ of the real open interacting system. In the following, we will assume that $\mathcal{F}_B(r, t)$ could be written as the divergence of $en(r, t)\vec{C}(r, t)/m$ as in 4. We want to point out that, one can in fact find *many* (possibly infinite) closed non-interacting quantum systems that reproduce the dynamics of the exact current and particle densities. One can show that this is *not* in contrast with the general theory of TDCDFT. Indeed, we can show that the *total* current in the closed KS system is uniquely determined by the total vector potential, given by the sum of the KS vector potential and $\vec{C}(r, t)$. However, the particle and the current density $\vec{j}(r, t)$ do not share this property, and we can find infinitely many closed non-interacting KS systems that reproduce these quantities. Indeed, in the proof of the Theorem 3 in Ref.¹⁷ it is stated that the vector

$$\vec{C}(r, t) = -\frac{m}{en(r, t)} \int d^3r \left(\frac{\partial n(r, t)}{\partial t} + \vec{\nabla} \cdot \vec{j}(r, t) \right) \quad (11)$$

can be uniquely determined by eqns (1) and (4) once a boundary condition in space that fixes an arbitrary function of time is assigned.

However, the above equation is not the unique solution. For instance, easily fulfilling the assigned boundary condition, one can add the curl of an arbitrary vector, $\vec{g}(r, t)$, to the “leakage potential” $\vec{C}(r, t)$ and still satisfy eqn (11). Indeed it is easily proven that $\vec{C}'(r, t) = \vec{C}(r, t) + (\vec{\nabla} \times \vec{g}(r, t))/n(r, t)$ still satisfies eqns 1 and 4, if $\vec{C}(r, t)$ satisfies the same equation. If we now continue with the proof and use $\vec{C}'(r, t)$ we arrive at a new vector potential $\vec{A}'_{KS}(r, t)$ that gives the same $n(r, t)$ and $\vec{j}(r, t)$ as the couple $\vec{A}_{KS}(r, t)$ and $\vec{C}(r, t)$. This ambiguity reflects the fact that we are trying to mimic the effect of a scalar function - the term $\mathcal{F}_B(r, t)$ in eqn 1 - with a vector function, $\vec{C}(r, t)$, without imposing strict boundary conditions (BCs) on $\vec{C}(r, t)$.

A simple solution to the aforementioned problem may appear by setting $\vec{\nabla} \times \vec{C}(r, t) \equiv 0$. However, it is important to realize that the imposition of certain boundary conditions on the dynamics of these quantities has a direct impact on the uniqueness of the results. For example, assuming that $\vec{C}(r, t)$ reaches a certain uniform limit when $|r| \rightarrow \infty$, might be *inconsistent*

with the bath operator acting on the true many-body system. Indeed, certain bath operators can be strongly non-local in space, effectively transferring charge from one region of space to another, with the two arbitrarily far from each other. Therefore, the BCs on $\vec{\nabla} \times \vec{C}(r, t)$ have not a clear physical origin or relation to any physical observable. Fixing their value to obtain one solution appears utterly arbitrary.

Notice that a similar problem appears also in the case of the standard theorem of TDDFT (see for example Ref.³¹) where the additional boundary condition $n(r)\vec{\nabla}\Delta V(r, t) \rightarrow 0$ when $|r| \rightarrow \infty$ is added to the proof. However, in this case, while in principle this condition is arbitrary and one may choose another condition, this choice is motivated by physical arguments that are valid for a wide range of systems. The same considerations instead do not apply to all the components of the vector $\vec{C}(r, t)$.

These ambiguities derive again from the attempt to find a mapping between the vector potential and the particle and current densities, when the continuity equation is not valid. In this attempt, one needs to include another scalar quantity to make that mapping meaningful. The choice of a vector quantity like $\vec{C}(r, t)$ in eqn (11) is ill-posed and leads to another ambiguity. On the other hand, if we are to gain any physical insight on the particle density, we need to obtain reliable approximations of the leakage potential. Instead, if one accepts that the quantity of interest is the current density, the leakage potential must be a functional of the current density and therefore we could solve the continuity equation for the particle density. For this reason, we can prove the following theorem (see below about some caveats regarding the use of a density matrix vs. a state vector formulation)

Theorem A (unique mapping from open to closed system): Consider the dynamics of a many-body system in contact with an external environment. Assume the evolution of the density matrix is given by Eq. (2) with the full many-body Hamiltonian (3). Then under reasonable physical assumptions, there exists a *closed* non-interacting auxiliary many-body Kohn-Sham system which starting from given initial conditions for the state of the many-body open system, evolves according to

$$i\partial_t|\Psi_{KS}(t)\rangle = \hat{H}_{KS}(t)|\Psi_{KS}(t)\rangle \quad (12)$$

with Hamiltonian

$$\hat{H}_{KS}(t) = \sum_i \left(\frac{\hat{p}_i + e\vec{A}_{KS}(\hat{r}_i, t)}{2m} \right)^2 \quad (13)$$

and reproduces the dynamics of the current density of the original many-body *open* system,

$$\vec{j}_{KS}(r, t) = \vec{j}(r, t). \quad (14)$$

The proof of this theorem is identical to those already present in the literature^{14,15,19}, we are therefore not reproducing it here

[†]. The only difference is that the current density of the original many-body open system follows the dynamics induced by the many-body Hamiltonian and by the external environment.^{14,15,19} The single-particle density can be obtained from eqn 1, once the leakage potential is written as a functional of $\vec{j}(r, t)$. The uniqueness of the closed quantum system then follows from the fact that two closed systems which share the same single-particle current density and initial conditions do coincide.²⁹

It is also interesting to note that the possibility of studying the dynamics of an open system by using a TDCDFT closed system, has been presented in the past. For example in³² the dynamics of a 2D electron gas coupled with the electrons confined in a 1D quantum well is investigated. The quantum well, via the Coulomb interaction, acts as an external forcing field that provides energy to the 2D gas. The dynamics of the latter is then described by an effective vector potential which contains no reference to the 1D well. One can show that the 2D electron gas will relax to a steady regime. A similar analysis has been performed for a 1D electron gas confined in a quantum well by using the Vignale-Kohn functional for TDCDFT.³³ In that case, the system relaxes to the ground state.^{34,35} The KS energy is lost to those degrees of freedom that the Vignale-Kohn functional does not take into account in describing the dynamics of the many-body system through some kind of common variable like the single-particle current density. It should not be surprising then that in this case the KS energy could be given a physical interpretation as the maximum work that could be extracted from the system.³⁵

Finally, we want to comment on a fundamental but important issue. As we have discussed at length in our previous publications,^{14,15} and at the beginning of this paper, one has two choices to describe an open quantum system: in terms of the density matrix or the state vector. These two formulations are generally equivalent, being the state vector formulation an unraveling of the density matrix one. However, the density matrix approach suffers from two drawbacks which do not make it a solid starting point for a formulation of DFT for open quantum systems. This is due to both the possible loss of positivity of the density matrix if an equation of motion of such quantity is employed with the Hamiltonian and/or bath operator(s) dependent on time,³⁶ and the fact that the KS Hamiltonian does depend on internal degrees of freedom. Starting from the master equation formulation of the same problem, one needs to exclude from the outset the possibility that the Hamiltonian of any auxiliary system with different interaction potential (and hence the KS Hamiltonian) depends on the internal degrees of freedom. Otherwise, for such a system no closed density-matrix equation can be obtained. In other words, one needs to start from an hypothesis that constitutes part of the final thesis. It is only when one starts from a stochastic Schrödinger equation for the *state*

[†] See for example the book by G. Giuliani and G. Vignale for a clear formulation¹⁰.

vector that one can prove that the *exact* KS Hamiltonian depends only on the average current density^{14,15}. In view of this criticism, we can easily reformulate the theorem A by starting from the stochastic Schrödinger equation as we have done in¹⁴.

In conclusion, we hope we have clarified many misunderstandings regarding a DFT for open quantum systems and its theoretical foundations. We have also shown some of the pitfalls of recent theories that have been advanced to improve on such theory. Such pitfalls originate from a simple, but yet not fully appreciated point in the DFT community, namely that one cannot map vector potentials with single-particle densities, a trivial consequence of the fact that there is no one-to-one correspondence between a vector and a scalar.

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